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Origin and early history

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Feature Article

The Lorenz-Lorentz Formula: Origin and Early History

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Abstract. Among the many eponymous formulae and laws met in textbooks in physics and chemistry, the Lorenz-Lorentz formula merits attention from a historical point of view. The somewhat curious name of this formula, which relates the refractive index of a substance to its density, reflects its dual origin in two areas of nineteenth-century physics, namely optics and electromagnetism. Although usually dated to 1880, the formula was first established in 1869 by L. V. Lorenz (optics) and subsequently in 1878 by H. A. Lorentz (electromagnetism). Apart from discussing the origin and priority of the Lorenz-Lorentz formula the paper outlines its early use in molecular physics and physical chemistry. During the late nineteenth century studies of molecular refractivity based on the formula proved important in a number of ways. For example, they led to estimates of the size of molecules and provided information about the structure of chemical compounds.

Keywords. L. Lorenz, H. A. Lorentz, optical refraction, Clausius-Mossotti formula, molecular refractivity.

1. INTRODUCTION

In 1902 the famous Dutch physicist Hendrik Antoon Lorentz (1853-1928) received the Nobel Prize in physics sharing it with his compatriot Pieter Zeeman. In his Nobel lecture delivered in Stockholm on “The Theory of Electrons and the Propagation of Light” he referred to the refraction of light and the recent insight that the phenomenon was due to vibrating electrical charges (electrons) in the refracting substance. Many years earlier he had succeeded in explaining on the basis of electromagnetic theory “the approximate change in the refractive index with the increasing or decreasing density of the body.” Lorentz continued: “When I drew up these formulae I did not know that Lorenz at Copenhagen had arrived at exactly the same result, even though he started from different viewpoints, independent of the electromagnetic theory of light. The equation has therefore often been referred to as the formula of Lorenz and Lorentz.”¹

It is the early history of this formula, variously called the Lorentz-Lorenz and the Lorenz-Lorentz formula or law, which is the subject of the present paper. In brief, the formula dates from 1869, when it was first proposed by

the relatively obscure Danish physicist Ludvig Valentin Lorenz (1829-1891) on the basis of experiments and optical theory. Nine years later it was independently derived on a very different basis by 25-year-old Lorentz in the Netherlands, his first major scientific work. The Lorenz-Lorentz formula, as I shall call it (and justify later), soon became accepted as an important law not only in optics and electromagnetic theory but also as an eminently useful tool in the new field of physical chemistry. Indeed, chemists embraced the formula at an early date, applying it in various ways to determine the molecular refractivity of chemical compounds and thereby to gain information on their constitution.

Ever since the 1880s the Lorenz-Lorentz formula has played a significant role in the physical sciences and it continues to do so. Still today, about 150 years after it was first proposed, it is an active research area in branches of physical chemistry, crystal chemistry and materials science.

The paper focuses on the period ca. 1870-1890 and in particular on the contributions of the little known Lorenz. A specialist in the mathematical theory of optics, contrary to Lorentz he never accepted Maxwell's electromagnetic theory and preferred to represent optical phenomena in terms of abstract wave equations with no particular physical interpretation. Although Lorenz, independently of Maxwell, suggested an innovative electrodynamic theory of light in 1867, he did not apply it to either the refraction or the dispersion of light (but see the end of Section 5).²

2. REFRACTIVITY AND DENSITY

The general idea that the refractivity index n of a transparent body is related to its density d was far from new at the time when Lorenz took up the subject. As early as in his revised edition of *Opticks* from 1718, Newton reported experiments on the refraction of light in a variety of substances ranging from air to olive oil and diamond (Figure 1).³ On the basis of these experiments he discussed the possibility of a "refractive power" of the form $(n^2 - 1)$ that varied proportionally to the body's density. About a century later Pierre Simon de Laplace, in his famous *Mécanique Céleste*, derived on the basis of the corpuscular theory of light what became known as the "Newton-Laplace rule." According to this rule

$$\frac{n^2 - 1}{d} \equiv \text{constant}$$

The refracting Bodies.	The Proportion of the Sines of Incidence and Refraction of the yellow Light.	The Square of BR, to which the refracting force of the Body is proportionate	The density and specific gravity of the Body.	The refractive Power of the Body in respect of its density.
A Pseudo-Topazius, being a natural, pellucid, brittle, hairy Stone, of a yellow Colour.	23 to 14	1'699	4'27	3979
Air.	3201 to 3200	0'000625	0'0012	5208
Glass of Antimony.	17 to 9	2'568	5'28	4864
A Selenitis.	61 to 41	1'213	2'22	5386
Glass vulgar.	31 to 26	1'4025	2'58	5436
Crystal of the Rock.	25 to 16	1'445	2'65	5450
Island Crystal.	5 to 3	1'778	2'72	6536
Sal Gemmae.	17 to 11	1'388	2'143	6477
Alume.	35 to 24	1'1267	1'714	6570
Borax.	22 to 15	1'1511	1'714	6716
Niter.	32 to 21	1'345	1'9	7079
Dantzick Vitriol.	303 to 200	1'295	1'715	7551
Oil of Vitriol.	10 to 7	1'041	1'7	6124
Rain Water.	529 to 396	0'7845	1'	7845
Gum Arabick.	31 to 21	1'179	1'375	8574
Spirit of Wine well rectified.	100 to 73	0'8765	0'866	10121
Camphire.	3 to 2	1'25	0'996	12551
Oil Olive.	22 to 15	1'1511	0'913	12607
Linseed Oil.	40 to 27	1'1948	0'932	12819
Spirit of Turpentine.	25 to 17	1'1626	0'874	13222
Ambar.	14 to 9	1'42	1'04	13654
A Diamond.	100 to 41	4'949	3'4	14556

Figure 1. Newton's measurements of the "refractive power" (column 5) relating the refractive index (column 2) to the density relative to water (column 4).

The Newton-Laplace rule was tested experimentally by J.-B. Biot and F. Arago in a work of 1806; the next year their investigations were continued by E. L. Malus. Although the formula agreed well with the experiments of the French scientists for gases, it failed miserably for liquid and solid bodies. Nonetheless it remained in use for many years, even after the corpuscular theory had been replaced by the wave theory of light.

A simpler and much better expression involving $(n - 1)$ instead of $(n^2 - 1)$ was proposed by an extensive series of experiments performed during the period 1858-1865 by the leading British chemist John Hall Gladstone (Figure 2) and his collaborator Thomas Dale.⁴ The two scientists established that for liquids,

$$(n-1)v = \frac{(n-1)}{d} = \text{constant},$$

where the quantity $v = 1/d$ is known as the body's specific volume. Gladstone and Dale referred to the quantity $R_{GD} = (n - 1)/d$ as the "specific refraction energy."⁵

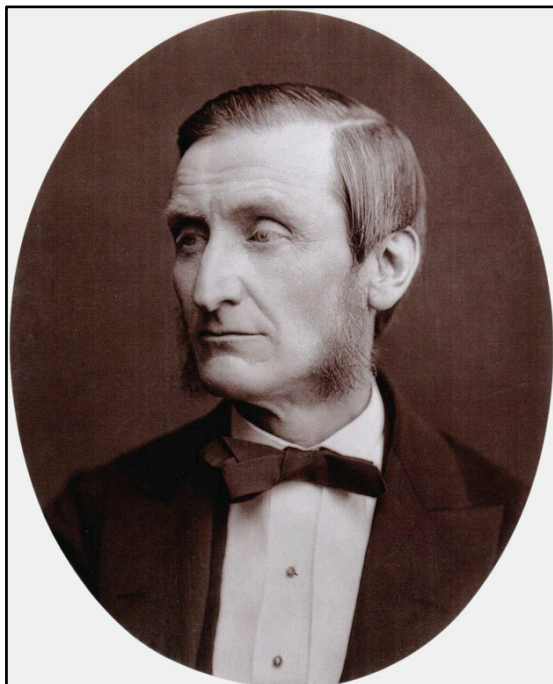


Figure 2. J. H. Gladstone (1827-1902). Source: https://en.wikipedia.org/wiki/John_Hall_Gladstone.

The relation was widely used for analyses of solutions, glasses and crystals, and determinations of the “Gladstone-Dale constant” are still part of modern mineralogy, geochemistry and materials science. However, the Gladstone-Dale constant is not a characteristic parameter of the refractive substance as it varies considerably with its physical state. Moreover, the Gladstone-Dale rule and other rules proposed in the mid-nineteenth century were basically empirical relations lacking a proper theoretical foundation. The rule was later provided with a theoretical justification, albeit this proved possible only by means of *ad hoc* hypotheses concerning the structure of the ether.⁶ It remained an empirical rule, practically useful but of limited scientific importance.

During the latter half of the nineteenth century several other refractivity-density relations were proposed, but these had very restricted applicability and were little more than extrapolations from a limited number of experiments. To mention but one example, in 1883, after the Lorenz-Lorentz law had been generally accepted, the German chemist W. Johst proposed that

$$\frac{\sqrt{n}-1}{d} = \text{constant}$$

The formula was discussed for a brief period of time after which it was forgotten.⁷

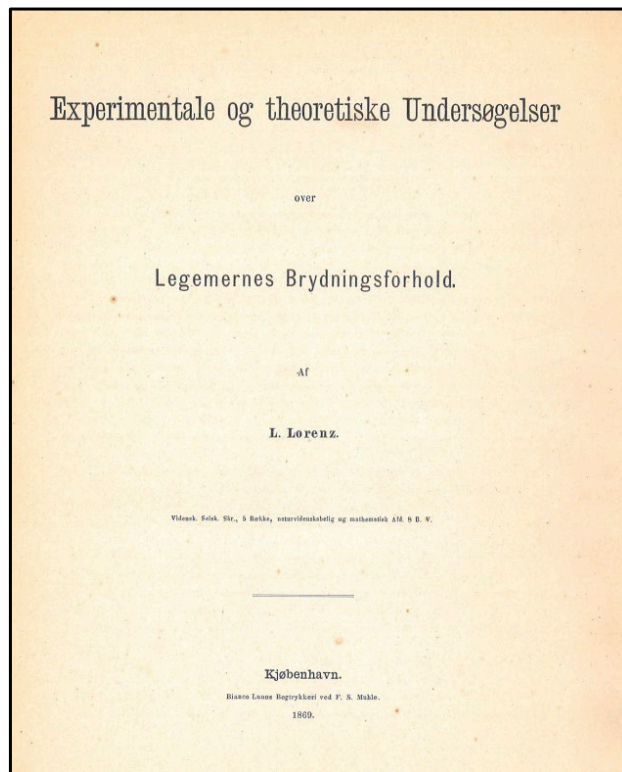


Figure 3. Lorenz's 1869 memoir on “Experimental and Theoretical Investigations on the Refractivity of Substances” published by the Royal Danish Academy of Sciences and Letters.

Ludvig V. Lorenz, a physics teacher at the Military High School in Copenhagen, was trained as a chemical engineer at the city's Polytechnic College. In the early 1860s he established a general, phenomenological theory of light from which he claimed that all optical phenomena could be deduced.⁸ The basis of the theory was three partial differential equations for a so-called light vector propagating with a velocity equal to the velocity of light and satisfying the condition that the waves were only transversal, not longitudinal. Lorenz had originally suggested that something similar to the Newton-Laplace rule would follow from his equations, but in 1869 he arrived at a different result.⁹ In a memoir of that year published by the Royal Danish Academy of Sciences and Letters, of which Lorenz had become a member three years earlier, he reported for the first time the Lorenz-Lorentz formula (Figure 3).

3. LORENZ'S OPTICAL ROUTE

From a series of elaborate experiments Lorenz established in his 1869 memoir a number of empirical formu-

lae, for example by measuring the refractive index for the yellow sodium light passing water at different temperatures t . In the interval between 0 °C and 30 °C he found that

$$n(t) = n(0) + [0.076t - 2.803t^2 + 0.002134t^3]10^{-6}$$

Thus, at a change in temperature of 10 °C the observed change in refractivity was found to be only of the order 0.01 per cent. Measurements of this kind had earlier been reported by the French physicist Jules Jamin in 1856, but Lorenz's data were more precise and in better agreement with later results.¹⁰

The refractive index depends on the wavelength and according to A.-L. Cauchy's semi-empirical dispersion formula of 1836 the dependency can be represented as

$$n(\lambda) = m + \frac{a_1}{\lambda^2} + \frac{a_2}{\lambda^4} + \frac{a_3}{\lambda^6} \dots,$$

where the symbols in the nominators are constants to be determined experimentally. The quantity m thus denotes the refractive index reduced to an infinite wavelength or zero frequency, $n(\lambda) \rightarrow m$ for $\lambda \rightarrow \infty$. If only the two first terms on the right hand are used, we have

$$n(\lambda) = m + \frac{a_1}{\lambda^2}$$

Then m can be calculated from measurements of two values of n corresponding to two wavelengths λ_1 and λ_2 with the result that

$$m = \frac{\lambda_1^2 n_1 - \lambda_2^2 n_2}{\lambda_1^2 - \lambda_2^2}$$

Having discussed his own data and those reported by other scientists, Lorenz concluded that m only depends on the density and that the temperature merely enters indirectly, namely by changing the volume and hence the density. He ended up with the following expression for water:

$$m(t) = 1.3219 + [21.05t - 2.759t^2 + 0.02134t^3]10^{-6}$$

Although Lorenz's experimental work was of unsurpassed precision (Figure 4), it did not differ essentially from similar measurements made in German and French laboratories. What distinguished his work from

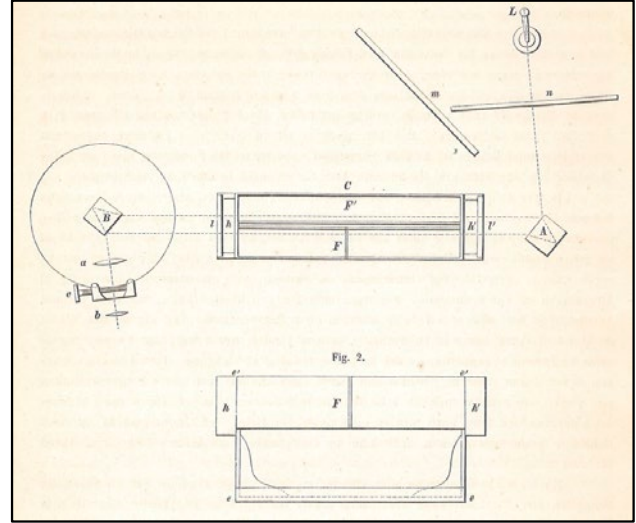


Figure 4. Lorenz's apparatus of 1869 for the determination of the refractivity-density relationship for liquids. In the tank C a thin tube with the liquid is enclosed between two mirror glasses I and I'. The two parts of the tank F and F' and the two small containers h and h' are filled with distilled water. The tank is mounted between two Jamin mirrors B and A formed as cubes. One of the light rays passes the tube while the other ray passes the water in the tank with the result that the interference lines are displaced. By measuring the number of displaced lines and the weight of the liquid Lorenz could relate the refractivity of the liquid to its density.

investigations made elsewhere was its connection to theory, which he covered in the second part of his treatise.

Proceeding from his fundamental wave equation Lorenz deduced in 1869 that the quantity $(m^2 - 1)v / (m^2 + 1)$ was given by a certain function that only depended on the distribution in space of the refractive substance. Since it was known from the Gladstone-Dale rule that $(m - 1)v$ was approximately constant, Lorenz concluded that the correct law of refractivity was given by what he called the "refraction constant," namely

$$\frac{m^2 - 1}{m^2 + 2} v = \text{constant} (= R_{LL})$$

This result was independent of the form of the molecule, he argued. However, for reasons of simplicity he assumed the refractive medium to be composed of optically homogeneous spherical molecules with m_i being their internal refractive index. With v_i being the specific proper volume of the molecules Lorenz could then write the law as

$$\frac{m^2 - 1}{m^2 + 2} v = \frac{m_i^2 - 1}{m_i^2 + 2} v_i$$

He further argued that the reduced refractive index was approximately constant and for a mixture consisting of k non-interacting components could be expressed as

$$\frac{m^2-1}{m^2+2}v = \sum_{j=1}^k \frac{m_j^2-1}{m_j^2+2}v_j$$

The observation turned out to have significant consequences for chemical investigations. For an isotropic substance consisting of only one kind of molecule he deduced the approximate relation

$$\frac{m^2-1}{m^2+2}v = P \left(1 - \frac{k^2}{v^2} \right)$$

Here P and k are two constants that depend on the molecular structure of the substance but not on its volume or temperature. For a gas, where v is large and m only slightly larger than 1,

$$m^2-1 \cong 2(m-1) \text{ and } m^2+2 \cong 3$$

Lorenz noted that the expression above approximates to

$$(n-1)v = \frac{3}{2}P$$

in agreement with the Gladstone-Dale formula. Moreover, the Lorenz expression also accommodates the Newton-Laplace rule since

$$\frac{n^2-1}{d} = R_{\text{LL}}(n^2+2) \cong 3R_{\text{LL}}$$

Only after a period of six years did Lorenz return to his studies of refraction, this time in a predominantly experimental paper where he reported measurements on oxygen, hydrogen, water vapour, ethanol, ether and other volatile liquids.¹¹ Lorenz's law of refractivity, derived as a theoretical consequence of his theory of light, received solid confirmation in 1880, when the Danish physicist Peter K. Prytz published extensive measurements on the refractive constants of a variety of liquids and vapours. The measurements showed convincingly that Lorenz's law was superior to the Gladstone-Dale rule.¹²

Prytz's 1880 paper in *Annalen der Physik und Chemie* was preceded by a paper in which Lorenz presented

a detailed summary of his two communications on optical refraction originally published in two sequels in the proceedings of the Royal Danish Academy.¹³ Using a new and simpler approach he derived the same expression for the relation between refractivity and density as in his earlier theory, namely a constant value of the ratio $(n^2-1)/d(n^2+1)$. It was only on this occasion that the international community of physicists became aware of his extensive work on the refractivity-density law. Since his memoirs of 1869 and 1875 were written in Danish, they were known only by scientists in Scandinavia.

4. OPTICAL REFRACTION AND MOLECULAR PHYSICS

Lorenz was convinced that optical research provided a method to obtain information about the size of molecules and their number in a volume or mass unit of a substance (Figure 5). In his 1875 paper he derived that for a substance composed of spherical and optical homogeneous molecules,

$$\frac{n^2-1}{n^2+2}v = \frac{n_i^2-1}{n_i^2+2}v_i(1+\delta),$$

With β being a measure of the molecular radius, he stated the δ quantity as

$$\delta = \frac{16}{5}\pi^2 \frac{n_i^2-1}{n_i^2+2} \frac{\beta^2}{\lambda^2}$$

According to Lorenz, it followed from experiments that for $\lambda = 589.3$ nm (sodium light) the value of δ was approximately 0.22.

Lorenz used this result for two purposes. First, he pointed out that since $\delta = \delta(\lambda^{-2})$ the expression explained dispersion, if only qualitatively, without relying on special assumptions about molecular forces or the structure of the ether. This contrasted with Cauchy's earlier theory of dispersion which relied on such assumptions and also was unable to explain why dispersion does not take place in void space. In Lorenz's very different theory, dispersion was a property of the heterogeneity of a substance and thus excluded dispersion in a vacuum. Importantly and contrary to other optical theories at the time, Lorenz's theory did not assume the existence of an ethereal medium.

The second use he made of his result was to estimate a lower limit to the size of molecules. In Lorenz's theo-

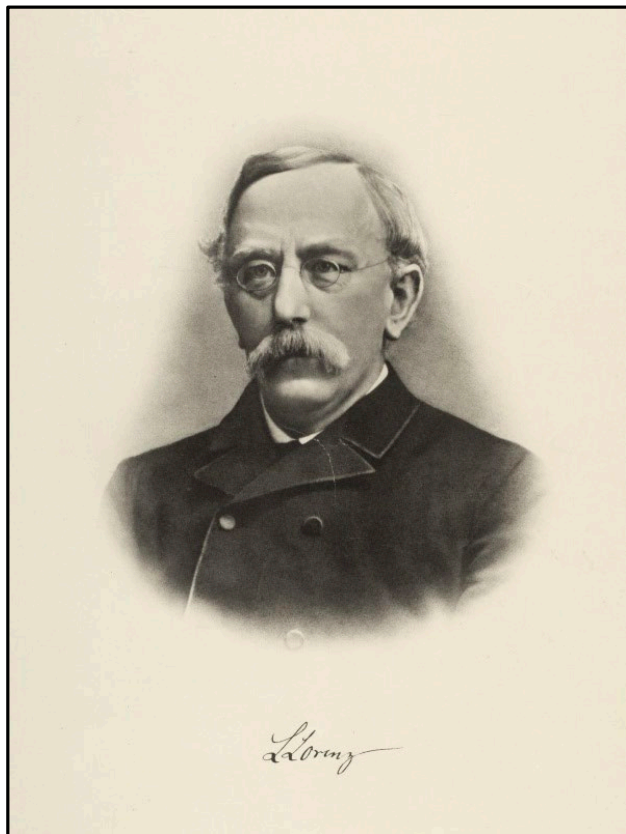


Figure 5. Ludvig V. Lorenz. Royal Library, Copenhagen, Picture Collection.

ry the quantity β was not literally the molecular radius but what he cautiously called “the radius of the molecular sphere of action, meaning the sphere surrounding a molecule within which there is an appreciable effect of the molecule’s influence on the velocity of light propagation.” This quantity is greater than the actual or material radius of the molecule. Since

$$\frac{n_i^2 - 1}{n_i^2 + 2} < 1$$

and with δ known, Lorenz was able to conclude that

$$\beta > 1.5 \times 10^{-8} \text{ m}$$

He was pleased to note that the German physicist Georg Hermann Quincke from recent measurements of viscosity and capillarity had found molecular radii agreeing with the limit inferred from the optical method.¹⁴

Using a different optical method based on the scattering of light on a small sphere, in an important memoir of 1890 Lorenz refined his value of β . He also estimated a value for the number of molecules in one millilitre of a gas, a quantity known as Loschmidt’s number (N_L) and named after the Austrian physicist and chemist Josef Loschmidt.¹⁶ The better known Avogadro number N_A is given by

$$N_A = 6.022 \text{ mole}^{-1} \cong 22.410^3 \times N_L$$

Lorenz reported $N_L = 1.63 \times 10^{19}$ while the modern value is $N_L = 2.688 \times 10^{19}$.

5. LORENTZ’S ELECTROMAGNETIC ROUTE

Lorenz’s law of refractivity is today referred to as the Lorenz-Lorentz law, or more commonly the Lorentz-Lorentz law, because H. A. Lorentz (Figure 6) derived the same result in 1878.¹⁷ Just the year before, he had been appointed professor of theoretical physics at the University of Leiden, at the tender age of 24. In his doctoral dissertation of 1875 Lorentz referred to the refractive index of various substances as given by their dielectric constants.¹⁸ He briefly discussed the Newton-Laplace formula relating the refractive index to the density but at the time without suggesting an improved law based on the electromagnetic theory.

Contrary to the Danish physicist, in his memoir of 1878 Lorentz obtained the improved law by combining the Clausius-Mossotti formula (see below) with the electromagnetic theory of light. However, he did not rely primarily on Maxwell’s theory but rather on an alternative action-at-a-distance theory proposed by Hermann von Helmholtz.¹⁹ At the time Maxwell’s field theory was generally considered to be very difficult, almost impenetrable. Although Lorentz appreciated the theory, he thought that it depended too much on unconfirmed hypotheses.

What is known as the Clausius-Mossotti formula was first proposed, if only implicitly, by the Italian physicist Ottaviano Fabrizio Mossotti in 1847. Much later the formula was stated by Rudolf Clausius in 1879 in an attempt to explain the dielectric properties of insulators on an atomistic basis. From a historical point of view the order of names is perhaps unfortunate, but “Mossotti-Clausius” is rarely used. With ϵ_r the material’s dielectric constant (or relative permittivity ϵ/ϵ_0 and α denoting the polarizability of the molecule, the Clausius-Mossotti formula for a unit volume with N molecules is

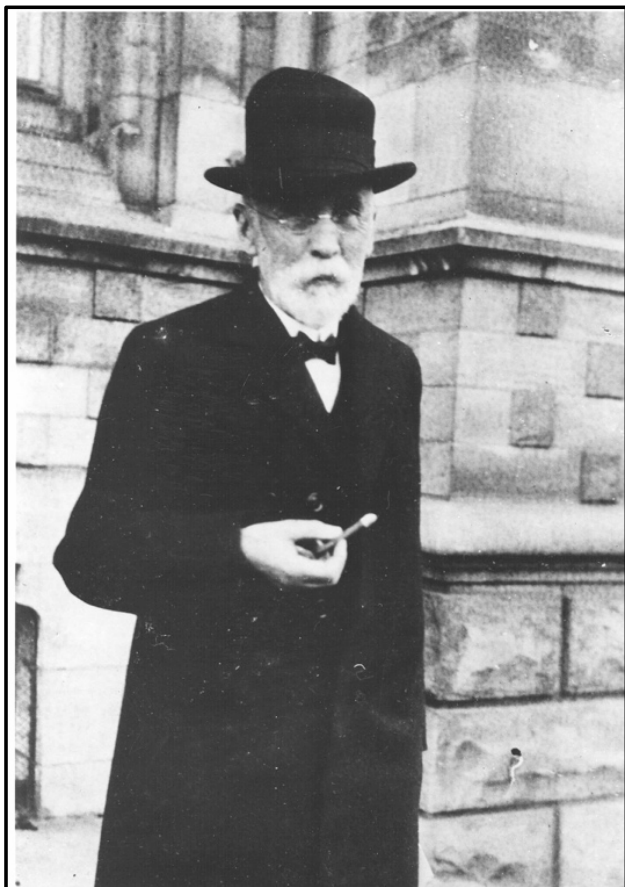


Figure 6. Hendrik A. Lorentz in 1927. Courtesy the Niels Bohr Archive, Copenhagen.

$$\frac{\varepsilon_r - 1}{\varepsilon_r + 2} = \frac{4\pi}{3} N\alpha$$

In modern literature this expression, which for $N = N_A$ is called the molar refractivity, is often used synonymously for the Lorenz-Lorentz formula. In a paper of 1910 on the theory of opalescence Einstein appropriately referred to it as the Clausius-Mossotti-Lorentz formula.²⁰ Modern physicists sometimes use the more cumbersome name Clausius-Mossotti-Lorentz-Lorentz (CMLL) formula.

The declared purpose of Lorentz's work was to construct a theory of the optical properties of matter, such as indicated by the title of his memoir, which in English reads "Concerning the Relation between the Velocity of Propagation of Light and the Density and Composition of Media." Contrary to his Danish near-namesake, Lorentz considered a molecular or atomic model in connection with his theory, namely that a molecule consists of an electric charge harmonically bound to the rest of the

molecule and characterised by its electric polarizability. He thought of the material molecule as being situated at the centre of a sphere or cavity, an idea which can also be found in Lorentz's paper of 1875.

Lorentz thus pictured the molecules as embedded in an all-pervading ether, which he, much like Maxwell, regarded as a dielectric substance. He emphasised the necessity of assuming inter-molecular space being filled with ether, a belief he stated was "not open to doubt." Lorentz, on the other hand, had dismissed the ether as superfluous and even "unscientific" in his electrical theory of light from 1867 and it played no role whatsoever in his optical theory two years later.

After a series of complex calculations Lorentz ended up with the following expression:

$$\frac{n^2 - 1}{(n^2 + 2)d} = \frac{\frac{4\pi}{3} \rho^3 (3 + 4\pi\varepsilon_0) - 4\pi\varepsilon_0 \frac{\rho^3}{\kappa}}{M(3 + 8\pi\varepsilon_0) \frac{\rho^3}{\kappa} - 8\pi\varepsilon_0}$$

Here ε_0 denotes the dielectric constant of the free ether, M is the mass of a molecule, d the density of the body, and κ is the ether's specific resistance according to Helmholtz's theory. The quantity on the right side of the equation is thus a constant for a particular transparent body. In the last part of his extensive 1878 memoir Lorentz compared his theoretical law of refraction with available experimental data from the literature. Unlike Lorentz, he did not perform experiments of his own.

In its modern formulation the Lorenz-Lorentz law is stated as a relation between the refractive index of a substance, a macroscopic quantity, and its polarizability α , a microscopic quantity:

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3} N\alpha,$$

When the polarizability is small, the equation reduces to

$$n^2 - 1 \cong 4\pi N\alpha \quad \text{or} \quad n - 1 \cong 2\pi N\alpha$$

In agreement with the Gladstone-Dale formula, this expression is valid for gases at normal pressure. It follows from the Lorenz-Lorentz theory that the polarization of a molecule in a solid body under the influence of an external electric field is not only determined by the strength of the field and the number of molecules per volume. There is also an effect due to the polarized

we find the same usage in the authoritative textbook on optics written by Max Born and Emil Wolf: “By a remarkable coincidence, the relation was discovered independently and practically at the same time by two scientists of almost identical names, Lorentz and Lorenz, and is accordingly called the Lorentz-Lorentz formula.”³¹

As an illustration of the popularity of the two terms, Google Scholar gives ca. 14,900 results for “Lorentz-Lorenz” and ca. 3,700 results for “Lorenz-Lorentz.” The preference for the first eponymous term can be seen as an example of a general tendency to associate a discovery with the name of a famous scientist even in cases where priority belongs to someone else.³² The Clausius-Mossotti formula is another example. Google Scholar also lists the number of references to the two *Annalen* papers of 1880, namely 192 references to Lorenz’s paper and 644 references to Lorentz’s.

7. A TOOL FOR PHYSICAL CHEMISTRY

After the refraction studies of Lorenz and Lorentz had become widely known they spurred a large number of experiments in molecular refractivity under various conditions. The overall result of this work was that the Lorenz-Lorentz law agreed far better with experimental data than competing formulae of an empirical nature. In a review paper of 1888 the British physicist Arthur William Rücker referred to the works of L. Lorenz and H. A. Lorentz as well as to Prytz’s experimental confirmation of the law named after them. Rücker found it of particular interest that the measurements of Lorenz and Prytz indicated that the value of $(n^2 - 1)/(n^2 + 2)$ did not depend on whether the substance was in a liquid or a vaporous state (Table 1). Having reviewed the experimental data Rücker concluded that “The results, on the whole, confirm the accuracy of the physical meaning of the expression $(n^2 - 1)/(n^2 + 2)$ and tend to show that the diameter of the molecule is the same in the liquid and gaseous state.”³³

Table 1. Data for the quantity $(n^2 - 1)/(n^2 + 2)$ obtained by Lorenz and Prytz. Source: Rücker (1888).

Substance	Formula	Work	Liquid	Vapour
Ethyl ether	$(C_2H_5)_2O$	Lorenz (1875)	0.30264	0.3068
Ethanol	C_2H_5OH	Lorenz (1875)	0.28042	0.2825
Water	H_2O	Lorenz (1875)	0.20615	0.2068
Methanol	CH_3OH	Prytz (1880)	0.2567	0.2559
Methyl acetate	$(CH_3)_2COO$	Prytz (1880)	0.2375	0.2399
Ethyl formate	C_2H_5COOH	Prytz (1880)	0.2437	0.2419

This was also the conclusion of the Austrian physicist Franz Exner, at the University of Vienna, who in 1885 stated that the Lorenz-Lorentz law had been “completely confirmed.”³⁴ As Exner pointed out, the law served as a key instrument for obtaining information about the size and constitution of molecules and the range of the unknown molecular forces. For the diameter of gas molecules he suggested the formula

$$D = C \frac{n^2 - 1}{n^2 + 2} \ell,$$

where C is an empirical constant and ℓ the mean free path of the molecules. Combining refractivity and diffusion measurements Exner found $D = 10^{-10}m$ for air molecules (N_2 , O_2) and $D = 2.7 \times 10^{-10}m$ for CS_2 vapour.

The subject of molecular refractivity belonged as much to chemistry as to physics. Indeed, refractivity studies had been part of theoretical chemistry many years before the Lorenz-Lorentz formula. The new formula further stimulated this kind of work which played a most important role in the new discipline of physical chemistry that emerged during the 1880s. When Lorenz and Lorentz figure in books on the history of chemistry, and not only in those on the history of physics, it is principally because of their role in the Lorenz-Lorentz formula.³⁵ By the turn of the century the formula and related refractivity studies had become a staple part of textbooks in physical chemistry.³⁶

The leading Swiss chemist Hans Heinrich Landolt and his German colleagues Wilhelm Ostwald and Julius Wilhelm Brühl were among those who applied the Lorenz-Lorentz formula to calculate the so-called molecular refractivity (or refractive power) of a particular substance. They defined this quantity as the product of the specific refractivity R_{LL} and the molecular weight M , that is, with n determined at a particular wavelength,

$$MR_{LL} = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d}$$

In cases where the Gladstone-Dale formula was used, the molecular refractivity was similarly given by

$$MR_{GD} = (n - 1) \frac{M}{d}$$

The monochromatic light used in most experiments was either the yellow sodium D line ($\lambda = 589 \text{ nm}$) or the red H_α line in the spectrum of hydrogen ($\lambda = 656 \text{ nm}$).

It turned out that in many cases the summation rule for mixtures could be carried over to chemical com-

pounds, such as suggested as early as 1863 in a paper by Gladstone and Dale.³⁷ If a compound consists of q_1, q_2, \dots elements with atomic weights μ_1, μ_2, \dots then the molecular weight is

$$M = q_1\mu_1 + q_2\mu_2 + \dots$$

According to the summation rule the molecular refractivity $r = R_{LL}$ is simply the weighted sum of the individual atomic refractivities given by

$$r_i = \frac{n_i^2 - 1}{n_i^2 + 2} \cdot \frac{\mu_i}{d_i}$$

That is,

$$\frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} = q_1\mu_1r_1 + q_2\mu_2r_2 + \dots$$

Experiments showed that although the rule was approximately correct for many compounds it was not universally true. In several cases the molecular refractivity differed substantially from the sum of the constituent atomic refractivities or, differently phrased, a particular atomic refractivity did not always have the same value. It was soon recognised that the molecular refractivity is influenced also by the constitution of the molecule as given by the arrangement of atoms and the presence of double and triple bonds.

The pioneer in this branch of optical chemistry was J. W. Brühl, who employed the Lorenz-Lorentz formula in a series of elaborate studies of inorganic as well as organic substances. By considering the refractivity values of compounds in homologous series he derived the corresponding values for double and triple bonds in molecules. He applied this method to the vexed and much-discussed question of the constitution of benzene, C_6H_6 . On the assumption of Kekulé's structural model with three single and three double bonds Brühl found a theoretical value for benzene's molecular refractivity that only differed 0.6% from the measured value. On the other hand, he concluded that alternative formulae suggested by H. Armstrong, A. von Baeyer, J. Thomsen and others did not agree with benzene's molecular refractivity (Figure 8).³⁸

While the Lorenz-Lorentz formula aroused great interest in the chemical community, none of the founders of the formula took much interest in the chemical applications. This is perhaps understandable in the case of Lorentz, who had neither interest in nor knowledge

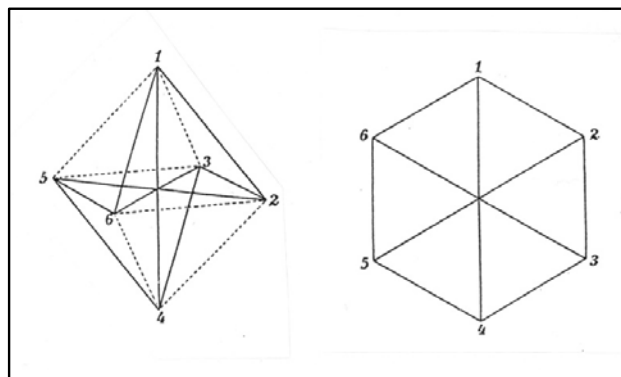
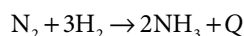


Figure 8. Based on thermochemical arguments the Danish chemist Julius Thomsen proposed in 1886 an octahedral model of benzene in which there were no double bonds. Thomsen's structural model was among those which Brühl dismissed as incompatible with refractivity data based on the Lorenz-Lorentz formula.

of chemistry, but it is more surprising in the case of the chemically trained Lorenz.

In fact, at the end of his 1880 paper Lorenz dealt with a number of chemical reactions during which the refractivity constant changed. From his own and others' experiments he suggested that the change in refractivity might constitute a measure of the chemical affinity in the same way as the change in heat (Q) did in the thermochemical Thomsen-Berthelot theory.³⁹ Lorenz suspected that exothermic processes were followed by a decrease in refractivity and endothermic processes by an increase. However, he admitted that the case of ammonia



was an exception to the rule. The molecular refractivity of NH_3 was known to be 0.3266 and Lorenz's measurements of a mixture of N_2 and H_2 in the mass ratio $\mu_N : 3\mu_H = 14 : 3$ resulted in 0.3116.

8. CONCLUSION

The Lorenz-Lorentz law is a general, non-trivial relationship between the refractive index of a substance and its density. The origin of the eponymous law – or perhaps better formula – is traditionally dated 1880 and considered an example of a simultaneous discovery made independently by the two physicists after which it is named. However, although Lorentz came to the law independently of Lorenz and the discovery was thus a “doublet,” it is not a simultaneous discovery since

the Danish co-discoverer formulated the law already in 1869, nine years before Lorentz. For this reason I propose that the law should properly be called the Lorenz-Lorentz law although most physicists and chemists prefer the other permutation.⁴⁰

The routes of the two physicists to the refractivity-density law were entirely different both as regards formalism and physical interpretation. And yet they arrived at exactly the same formula. In the physical sciences it is not unusual that the same result can be derived in different ways and therefore is not uniquely determined by the underlying theory. From a modern point of view the theory behind the Lorenz-Lorentz law is simply Maxwell's theory of electromagnetism, but Lorentz's original formulation had nothing to do with that theory. Aware of the dual origins of the law, Wilhelm Ostwald commented that "this agreement between two completely different approaches increases the probability that the result has a more general significance than if it were based on one or the other of the theoretical foundations."⁴¹

Whatever its theoretical background and interpretation, the Lorenz-Lorentz law was eminently successful and instantly applied to the study of molecular refractivity and related branches of chemistry, physics and materials science. By the early twentieth century it was predominantly a resource for the new generation of physical chemists rather than a topic belonging to theoretical physics.

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